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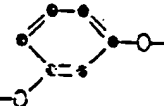
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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification:</b> C08G 63/18	<b>A1</b>	<b>(11) International Publication Number:</b> WO 79/01040 <b>(43) International Publication Date:</b> 29 November 1979 (29.11.79)
<b>(21) International Application Number:</b> PCT/US79/00214 <b>(22) International Filing Date:</b> 5 April 1979 (05.04.79) <b>(31) Priority Application Number:</b> 903,437 <b>(32) Priority Date:</b> 8 May 1978 (08.05.78) <b>(33) Priority Country:</b> US  <b>(71) Applicant:</b> EASTMAN KODAK COMPANY [US/US]; 343 State Street, Rochester, NY 14650 (US).  <b>(72) Inventors:</b> JACKSON, Jr., Winston, Jerome; 4408 Greensprings Circle, Kingsport, TN 37664 (US). MORRIS, John Craft; 359 Summerville Road, King- sport, TN 37663 (US).		<b>(74) Agent:</b> KLINE, William, H., J.; Eastman Kodak Compa- ny, 343 State Street, Rochester, NY 14650 (US).  <b>(81) Designated States:</b> DE (European patent), FR (Euro- pean patent), GB (European patent), JP.  <b>Published with:</b> <i>International search report</i>
<b>(54) Title:</b> LIQUID CRYSTAL COPOLYESTERS  <b>(57) Abstract</b> <p>Liquid crystal copolyesters having melting points low enough to allow the copolyesters to be melt-processed in conventional equipment. The copolyesters are prepared from terephthalic acid, 2,6-naphthalenedicarboxylic acid, a diacyl ester of hydroquinone and a diacyl ester of resorcinol and contain the following divalent radicals:</p> <div style="text-align: center;">           </div>		

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LIQUID CRYSTAL COPOLYESTERSTechnical Field

This invention relates to liquid crystal copolyesters having the high mechanical properties of liquid crystal copolyesters and melting points low enough to allow the copolyesters to be melt-processed into useful articles using commercially available equipment.

10 Background of the Invention

Liquid crystal copolyesters that are all-aromatic have excellent mechanical properties. Examples of these polyesters are the copolyesters prepared from terephthalic acid, 2,6-naphthalenedicarboxylic acid, hydroquinone and resorcinol. U.S. Patents 3,160,602 and 3,778,410 describe processes that can be used to prepare these copolyesters. It has been difficult to use these copolyesters because the melting points of the polymers have been so high that the polymers cannot be melted and formed into useful articles in conventional processing equipment.

Disclosure of Invention

We have found that certain all-aromatic copolyesters prepared from terephthalic acid, 2,6-naphthalene dicarboxylic acid, hydroquinone and resorcinol have melting points that are low enough to permit the copolyesters to be processed into useful articles, such as fibers and molded articles, in conventional equipment.

30 The copolyesters of this invention are prepared from terephthalic acid, 2,6-naphthalenedicarboxylic acid, a diacyl ester of hydroquinone and a diacyl ester of resorcinol and can be defined as copolyesters having molecular weights suitable for forming fibers and  
35 containing the following divalent radicals:



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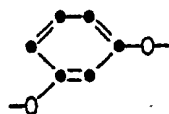


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and

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In our copolyesters the range of terephthalic acid is from 20 to 50 mole percent, based on the total moles of terephthalic acid and 2,6-naphthalenedicarboxylic acid combined. Since the range of terephthalic acid is based on the sum of the moles of terephthalic acid and 2,6-naphthalenedicarboxylic acid, at 20 mole percent terephthalic acid the copolyesters have 80 mole percent 2,6-naphthalenedicarboxylic acid and at 50 mole percent terephthalic acid the copolyesters have 50 mole percent 2,6-naphthalenedicarboxylic acid.

In preferred copolyesters the range of terephthalic acid is from 30 to 45 mole percent, based on the total moles of terephthalic acid and 2,6-naphthalenedicarboxylic acid combined.

Also in our copolyesters the amount of resorcinol is from 20 to 65 mole percent, based on the total moles of hydroquinone and resorcinol combined. Thus, at 25 mole percent resorcinol, the copolyesters have 75 mole percent hydroquinone, and at 65 mole percent resorcinol the copolyesters have 35 mole percent hydroquinone.

In preferred copolyesters the range of resorcinol is from 30 to 50 mole percent, based on the total moles of resorcinol and hydroquinone.

The precise manner in which the melting points of the copolyesters of the invention are unexpectedly lower than the melting points of similar copolyesters is illustrated in the Figure.

5 In the Figure the amount of terephthalic acid, based on the total moles of terephthalic acid and 2,6-naphthalenedicarboxylic acid, has been plotted on the abscissa. The temperature in degrees Centigrade has been plotted on the ordinate. Melting points have been  
10 plotted for copolyesters of the invention, containing a quantity of terephthalic acid in the range of 20 to 50 mole percent, based on the total moles of terephthalic acid and 2,6-naphthalenedicarboxylic acid. Suitable curves have been drawn through the data points  
15 for copolyesters containing the same amount of resorcinol. For example, the lowermost curve drawn through the closed circular data points represents the melting points of copolyesters containing 40 mole percent resorcinol, based on the total moles of hydroquinone and  
20 resorcinol combined.

The data for the copolyesters of the invention were obtained by preparing each of the copolyesters using a process known in the art and then determining the melting points of each copolyester.

25 The copolyesters of the invention were prepared by an acidolysis procedure whereby terephthalic acid, 2,6-naphthalenedicarboxylic acid, a diacyl ester of hydroquinone and a diacyl ester of resorcinol were reacted under an increasing temperature ranging up to  
30 340-380°C. and a decreasing pressure to form a high molecular weight polymer. As a specific example, the following procedure was used to prepare a copolyester from 40 mole percent terephthalic acid and 60 mole percent 2,6-naphthalenedicarboxylic acid, based on the  
35 moles of terephthalic acid and 2,6-naphthalenedicarboxylic acid combined, and 60 mole percent hydroquinone and

40 mole percent resorcinol, based on the moles of hydroquinone and resorcinol combined.

A mixture of 33.2 g. (0.20 mole) terephthalic acid, 64.8 g. (0.30 mole) 2,6-naphthalenedicarboxylic acid, 38.8 g. (0.20 mole) resorcinol diacetate, and 66.6 g. (0.30 mole) hydroquinone dipropionate was placed in a 500-ml. flask equipped with a stirrer, short distillation column and an inlet for nitrogen. The flask was evacuated and purged three times with nitrogen and dried at 100-110°C. for 30 minutes at 0.3 mm. pressure before being immersed in a bath at 275°C. After the mixture was stirred for 30 minutes at 280°C., the temperature was raised to 300°C. for 30 minutes and then to 325°C. for 30 minutes. Finally the temperature was raised to 355°C. for 25 minutes and a vacuum of 0.5 mm. was applied. The polymerization was complete within 20 to 30 minutes. The tough, fibrous, opaque polymer obtained had a softening point of 332°C. and a melting point of 341°C. Fibers with tenacities >3 g./denier can be melt spun at 360°C. Heat-treated fibers had tenacities of 10 g./denier and higher.

The other copolyesters containing different amounts of 2,6-naphthalenedicarboxylic acid, terephthalic acid, hydroquinone and resorcinol were prepared by a similar procedure but using slightly different reaction temperatures because of differences in melting points.

Solid-phase polymerization also may be used to increase the molecular weight of the copolyesters of the invention by heating polymer particles in an inert atmosphere or under reduced pressure at a temperature below that at which the particles will become tacky and tend to fuse together. Since this thermal treatment may give polymers with increased crystallinity and melting points, compared to melt phase



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polymerization, melt phase polymerization is generally preferred. Solid-phase polymerization is preferred, however, if the melting point is above 380°C.

5 The melting points of the copolyesters of the invention were determined with a differential scanning calorimeter.

10 The accompanying Figure shows that the melting points of the copolyesters of the invention containing 20 to 50 mole percent terephthalic acid and 20 to 65 mole percent resorcinol are unexpectedly lower than the melting points of copolyesters containing less than 20 or more than 50 mole percent terephthalic acid. For example, consider the copolyester which contains a constant value of 40 mole percent resorcinol and is represented by the lower curve connecting the closed circular data points. When the amount of terephthalic acid is below 20 mole percent, the melting point is above 400°C. As the amount of terephthalic acid is increased, the melting point falls and reaches a minimum value of 20 330°C. at 30 mole percent terephthalic acid. As the amount of terephthalic acid is increased, the melting point increases and is 385°C. at 50 mole percent terephthalic acid.

25 Although the details of the reduction in melting point have been discussed only for the copolyesters containing 40 mole percent resorcinol, the same lowering of the melting point applies to the other copolyesters of this invention. For example, the melting point of the copolyesters containing 20 and 60 mole percent resorcinol is also substantially lowered when from 30 20 to 50 mole percent terephthalic acid is used. Although melting point data is not plotted for copolyesters containing less than 20 mole percent terephthalic acid, it is clear from the shape of the curve melting 35 points are above 400°C.



A wide variety of diacyl esters of hydroquinone and resorcinol can be used to prepare the copolyesters of this invention. Examples of diesters include the diacetate, dipropionate, dibutyrate and dibenzoate.

5 The diacetate and dipropionate are preferred.

The copolyesters of this invention can contain minor amounts of other naphthalenedicarboxylic acid isomers in addition to the 2,6-isomer. Also, minor amounts of dicarboxylic acids other than terephthalic acid and diols other than hydroquinone can be used. The copolyesters of this invention can also contain nucleating agents, fillers, pigments, glass fibers, asbestos fibers, antioxidants, stabilizers, plasticizers, lubricants, fire-retardants, and other additives.

15 The inherent viscosity of the copolyesters of this invention cannot be determined because the copolyesters of this invention are insoluble in typical solvents used for determining inherent viscosity. Although the inherent viscosity of the copolyesters of the invention has not been measured, the molecular weights of the copolyesters of the invention are high enough to be in the fiber-forming range. The minimum fiber-forming molecular weight of the copolyesters is about 5,000. In most cases copolyesters of the invention have molecular weights above 8,000 and can have molecular weights as high as 20,000 and in some instances the molecular weights can range up to 25,000 or even higher.

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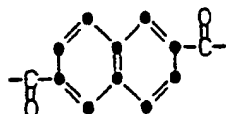
We Claim:

1. Copolyesters having a fiber-forming molecular weight and containing the following divalent radicals:

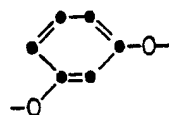
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the copolyesters being characterized by the amount of

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being from 20 to 50 mole percent,

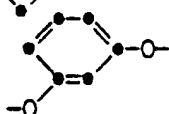
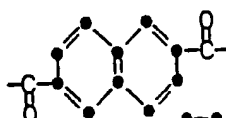
based on the total moles of



and

combined, and the amount of

25



being from 20 to 65 mole percent,

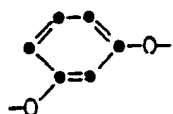
based on the total moles of



and

combined.

30



2. The copolyester of Claim 1 wherein the

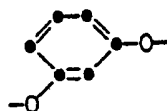
range of the amount of



is from 30 to

35

45 mole percent and the range of the amount of



is from 30 to 50 mole percent.

# INTERNATIONAL SEARCH REPORT

WO 79/01040

International Application No PCT/US79/00214

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) \*

According to International Patent Classification (IPC) or to both National Classification and IPC

INT.CL. C08G 63/18;

U.S. CL. 528/190

## II. FIELDS SEARCHED

Minimum Documentation Searched \*

Classification System

Classification Symbols

US

528/190; 528/193; 528/194

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched \*

## III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>14</sup>

Category *	Citation of Document, <sup>15</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
X	US, A, 3,160,602, PUBLISHED 08 DECEMBER 1964, KANTOR ET AL.	1-2
X	US,A, 3,778,410, PUBLISHED 11 DECEMBER 1973 KUHFUSS ET AL.	1-2
A	US, A, 4,066,620, PUBLISHED 03 JANUARY 1978 KLEINSCHUSTER ET AL.	1-2
X,P	US, A, 4,118,372, PUBLISHED 03 OCTOBER 1978 SCHAEFGEN	1-2
X,E	US,A, 4,156,070, PUBLISHED 22 MAY 1979 JACKSON, JR, ET AL.	1-2
X,E	US,A, 4153,779, PUBLISHED 08 MAY 1979 JACKSON, JR. ET AL.	1-2

\* Special categories of cited documents: <sup>16</sup>

"A" document defining the general state of the art

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filing date

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to in the other categories

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"T" later document published on or after the International filing  
date or priority date and not in conflict with the application,  
but cited to understand the principle or theory underlying  
the invention

"X" document of particular relevance

## IV. CERTIFICATION

Date of the Actual Completion of the International Search \*

07 AUGUST 1979

Date of Mailing of this International Search Report \*

13 AUG 1979

International Searching Authority \*

ISA/US


Signature of Authorized Officer <sup>20</sup>

LESTER L. LEE



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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> D02G 3/00, B32B 9/00, 25/20, C08L 75/00, 83/00, C08K 3/20	<b>A1</b>	<b>(11) International Publication Number:</b> WO 94/16129 <b>(43) International Publication Date:</b> 21 July 1994 (21.07.94)
<b>(21) International Application Number:</b> PCT/US94/00574 <b>(22) International Filing Date:</b> 13 January 1994 (13.01.94) <b>(30) Priority Data:</b> 08/003,780 13 January 1993 (13.01.93) US <b>(71) Applicant:</b> PPG INDUSTRIES, INC. [US/US]; One PPG Place, Pittsburgh, PA 15272 (US). <b>(72) Inventors:</b> WATKINS, Johnson, C.; 4 Albergar Drive, San Clemente, CA 92672 (US). SWISHER, Robert, G.; 172 Gordon Street, Pittsburgh, PA 15218 (US). <b>(74) Agents:</b> STACHEL, Kenneth, J.; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 (US) et al.	<b>(81) Designated States:</b> CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>  	
<b>(54) Title:</b> CHEMICALLY TREATED INORGANIC OXIDE FIBERS WITH THERMAL STABILITY SUITABLE FOR HIGH TEMPERATURE POLYMERS  <b>(57) Abstract</b>  Inorganic oxide substrates treated with an aqueous chemical treating composition having at least one organo alkoxide or hydroxide of a metal selected from titanium and zirconium either with a select combination of film forming polymers and/or with one or more organo- functional silane coupling agents. The combination of the titanium or zirconium coupling agent and the silane coupling agent can be as two distinct compounds.		

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GA	Gabon				



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CHEMICALLY TREATED INORGANIC OXIDE FIBERS WITH  
THERMAL STABILITY SUITABLE FOR HIGH TEMPERATURE POLYMERS

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This application is a continuation in part of application Serial No. 07/771,897, filed October 7, 1991, which is a continuation of application Serial No. 07/283,091, filed December 12, 1988.

10

The present invention is directed to chemically treated or "sized" fibers of organic oxides such as silica, alumina, calcium oxide, magnesium oxide and the like, for instance, those present in glass fibers and ceramic fibers. These sized fibers can display good thermal properties for use as reinforcement and fillers for numerous matrix polymer and especially for the high temperature stable or high temperature processable matrix polymers.

15

Fiber reinforced plastics (FRP) have utilized inorganic oxide fibers like glass fibers to reinforce thermosetting and thermoplastic polymers for the ultimate production of various molded products. Typically, the production of glass fiber reinforcement involves chemically treating the glass fibers with a sizing composition to increase the oleophilic character of the glass fibers and to protect the glass fibers from external abrasion and intrafilament abrasion during formation and processing. Developments in the area of matrix polymers for the FRP industry resulted in polymers designed for use at higher temperatures to expand the utilization of FRP products. For instance, matrix polymers such as polyethersulfone (PES), polyphenylene sulfide (PPS), polyaromatic ketones like polyetheretherketone (PEEK) and polyetherketone (PEK) and polyetherketone-ketone (PEKK) and polyketone (PAEK) and amorphous, aromatic polyesters (polyarylates) are just a few examples of matrix polymers developed or in the development stage having good heat or temperature resistance. The glass and ceramic fibers by

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- 2 -

themselves have good heat or temperature resistance so that in a composite of FRP a weak link in the armor of thermal resistance may be the chemical treatment or sizing on the fibers.

5           The sizing composition typically includes one or more film forming polymers, a coupling agent like an organo-functional silane coupling agent, a fiber lubricant, possibly emulsifiers for the film forming polymer, and perhaps wetting agents, all of which are usually present in an aqueous  
10 solution for application to the fibers.

It is an object of the present invention to provide chemically treated (sized) inorganic oxide fibers like glass fibers having improved properties like better adhesion or thermal and temperature resistance for use in the high  
15 temperature processed or high temperature resistant polymeric matrices, although the sized fibers can also be used in other polymeric matrices.

#### Summary of the Invention

The aforementioned objects and others gleaned from  
20 the following disclosure are furthered by the present invention of the inorganic oxide substrates treated with the sizing composition. This composition has an alkoxide or hydroxide of a titanium and/or zirconium metal where the compound has organic functionality. This organoalkoxide or  
25 organohydroxide titanium or zirconium is present along with polyurethane and epoxy film forming polymers and/or an organo functional silane coupling agent as an additional coupling agent or in a blend, mixture, reaction product with the silane coupling agent. The amount of the organofunctional silane  
30 coupling agent as a separate coupling agent can range up to around and including an effective coupling agent amount.

The amount of the organoalkoxide or organohydroxide titanium or zirconium is generally an amount greater than 10 parts per 100 parts of any film forming polymer and an amount  
35 to give a ratio of an amount with the organosilane, when

- 3 -

present, in the range of about 2:1 to about 1:2. Also there can be present at least one film forming polymer that can be essentially free of polyvinylacetate homopolymer and polyacrylic homopolymers and copolymers where the amount is an effective film forming amount. Also present can be at least one fiber lubricant in an effective lubricating amount. Also present is a carrier for application of the size to the substrate, and the carrier is present in an effective application amount.

Another aspect of the present invention is where the chemically treated inorganic oxide substrates are fibers having a volatile reduced residue of an aqueous size composition. In one aspect of the invention, at least one film forming polymer is present that is a polyurethane film forming polymer, and also present are: the fiber lubricant that is essentially free of large amounts of propylene oxide moieties. Also, the ratio of the organofunctional silane coupling agent, when present, to the organo alkoxide of titanium and/or zirconium is in the range of around 6:1 to around 1:6, and the carrier is water. Optionally, an additional film forming polymer can be present such as an epoxy film forming polymer generally to give a ratio of the amounts of the epoxy to polyurethane film forming polymers of around 10:1 to around 1:10. When this combination of film forming polymers is present, the organofunctional silane coupling agent need not be present, and the amount of the organo alkoxide or hydroxide of titanium and/or zirconium is present in an effective coupling agent amount. Otherwise than with this combination of film forming polymers, the organofunctional silane is generally present.

The chemically treated (sized) inorganic oxide fibers and especially glass fibers of the present invention find suitability in reinforcing polymeric matrices and especially the higher melting polymers or more thermally resistant polymers. Nonexclusive examples of these include:

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(PPS), (PPS), (PEI), polyarylates, (PES), (PEEK), (PAEK), (PEK), (PEKK) and the like. Other matrix polymers like poly(butylene terephthalate) polyamides may be reinforced with the sized fibers of the present invention.

5                   Detailed Description of the Invention

The film forming polymer that can be utilized in the chemical treating composition in the present invention is any film forming polymer that forms a film upon evaporation of volatiles or upon curing by the addition of a curing agent. Those that are especially useful are essentially free of unmodified polyvinylacetate homopolymer and polyacrylates. For instance, the removal of the volatiles or the curing can occur when the treated fibers or substrates are heated. The film that is formed need not be a vertically self-supported film, but it should at least be a discontinuous coating of a perceivable thickness. The film forming polymer can be a liquid or an emulsion, suspension or dispersion of the polymer in a carrier compatible liquid. For instance, the emulsion can be an oil-in-water type emulsion where, when the water and any other volatiles are removed, the film of the polymer is formed.

Nonexclusive examples of the film forming polymer include: polyurethane polymers, epoxy polymers, epoxy-polyurethane copolymers, polyester polymers, bisphenol A thermoplastic polyesters, polyvinylpyrrolidone, and the like. Suitable epoxy polymers present in the form of an oil-in-water dispersion or emulsion, hereinafter referred to as an emulsion, include those discussed in U.S. Patent No. 4,615,946 (Temple), which is incorporated herein by reference. One such epoxy polymer emulsion is that available from Interez, Inc., under the trade designation "EPI-REZ CMD 35201" material. This epoxy resin has an epoxy resin dispersion which has 60 percent nonvolatiles and the only volatile material is water and the dispersion has a weight per epoxide of approximately 530, a pH of 8.3, and an average particle size between 1 and 4

- 5 -

microns. The most suitable epoxy resin is the epoxy resin dispersion available from Interez, Inc., under the trade designation CMD-W-60 5520 which has a percent solids of  $60 \pm 2$  and a viscosity LVT No. 4 at 30 rpm of  $10,000 \pm 2,000$ .

5 Another suitable film forming polymer that can be used is one or more polyurethane polymers. By the use of the term polyurethane, it is meant to include reaction products of organic compounds having at least two active hydrogens and di and/or polyisocyanates, wherein the resulting polymer is a  
10 curable polyurethane or polyurethane urea type polymer through removal of volatiles or curing by a curing agent. For instance, the organic compounds with at least two active hydrogens is a polyol such as a polyester polyol or polyether polyol and most preferably, a polyol which is linear.  
15 Examples of polyester-based polyurethane elastomers include those where the polyester is prepared from carboxylic acid such as adipic and the glycol portion can be selected from such materials as ethylene glycol, 1,3-propylene glycol, 1,3-butylene glycol and 1,4-butylene glycol. Further examples of  
20 polyfunctional polyesters which can be used are those based on phthalic anhydride, adipic acid, ethylene glycol, trimethylol propane, and the like. A slight amount of branching of the polyol can be tolerated but the degree of functionality or branching of the polyol should be kept to a minimum since  
25 increased branching results in films that are tougher, harder and less flexible. The di or polyisocyanates generally used to form the polyurethane are selected from aromatic, aliphatic and mixtures thereof, isocyanates but the aliphatic isocyanates are preferred. Examples of the polyisocyanates  
30 that can be used include: the aromatic isocyanate of toluene diisocyanate and the aliphatic isocyanates such as hexamethylene diisocyanate, methylcyclohexylene diisocyanate, dicyclohexyl methane diisocyanate, lysine diisocyanate where the aromatic group is methyl or ethyl, bis(2-isocyanato ethyl)  
35 fumaric, bis(2-isocyanato ethyl) carbonate and dimeryl

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diisocyanate, where the organic group is essentially a C<sub>36</sub> hydrocarbon radical. Another isocyanate that may be used is 4,4'-diphenyl methane diisocyanate. The polyurethane polymer can be made as an uncurable or as a curable material by any method known to those skilled in the art, for instance, additional monomers like diisocyanate, polyols or epoxies can be added to the polymer and/or a curable moiety can be introduced into the polymer. The polyurethane polymers can be produced by any one-shot or single step method known to those skilled in the art or by the two step chain extension process utilizing linear or lightly branched polyols with the necessary molar portions of a diisocyanate known to those skilled in the art to produce a water dispersible polyurethane.

Specific nonexclusive examples of commercially available polyurethane polymers in an oil-in-water emulsion that can be used include a blend of polyester based polyurethane dispersions such as Witcobond W-290-H, available from Witco Chemical Corporation and XW-110 dispersion available from Mobay Chemical Corporation a former subsidiary of Bayer U.S.A. Inc., now known as Miles Inc. The XW-110 material is a fully reacted polyurethane dispersed in water/N-methyl-2-pyrrolidone and contains little or no free isocyanates. The dispersion has a hazy off-white appearance with a 35 percent solids level and a density of 8.7 lb/gal. The viscosity at 25°C (77°F) in cps is 130, and the surface tension in dynes/cm is 41. The film properties include: clear appearance, 6,600 psi tensile strength, 170% elongation at break, 5200 psi modulus at 100% elongation and 5700 psi yield modulus. The Witcobond W-290-H polyurethane has a milky white appearance, is aliphatic in type with a 65 percent solids level with an anionic charge and with a particle size of around 2 micrometers and with a pH at 25°C (77°F) of 7.5 and with a viscosity as measured by Brookfield LVF in cps of 200 and with a surface tension of 42 dynes/cm. The film

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properties of the 290H material are: 4500 psi tensile strength, 720 percent elongation and moduli of 250 psi at 100%, 540 psi at 300% and 1550 psi at 500%.

In addition a combination of film forming polymers  
5 may be used in the form of a combination of two distinct emulsions, suspensions or dispersions or solutions or as a mixture of these or as copolymers of the functional moieties such as epoxy polyurethane copolymers. For instance, when the treated substrates are reinforcement for PPS, PEI, polyamides  
10 and polybutylene terephthalate, the polyurethane polymer can be the sole film forming polymer in the size composition. Also, other film forming polymers may be present to give further enhanced properties, but the polyurethane is sufficient to provide a thermally stable, sized reinforcement.  
15 A suitable combination of the film forming polymers is a polyester urethane polymer used in conjunction with an epoxy-containing film forming polymer or their emulsions, dispersions, suspensions or solutions. When the emulsions of both of these film forming polymers are used, it has been  
20 found that a suitable ratio of the two to yield an effective film forming amount of total film forming polymer is around 4:1 to around 1:1 of the epoxy containing polymer to the polyurethane polymer. Additional amounts of the epoxy polymer may reduce some handling characteristics of chopped sized  
25 glass fibers. Specifically the filamentation resistance may be decreased, while additional amounts of polyurethane polymer may result in less thermal resistance of a reinforced composite. Generally, the amount of the film forming polymer is an effective film forming amount. This amount results in  
30 the film residue upon evaporation of the volatiles or curing of the curing agent with film forming polymer. The effective film forming amount generally ranges from around 1 to around 25 weight percent of the total size including the carrier, although higher amounts are possible for higher solids  
35 applications. For instance, when an oil-in-water emulsion

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with a film forming polymer is present in an aqueous size, the amount of the emulsion on a solids basis is around 5 to around 90 weight percent of the solids of the aqueous chemical treating composition. Generally, the percent solids of the oil-in-water film forming emulsion is in the range of about 10 to about 80 weight percent of the emulsion.

Additionally, the chemical treating composition has at least one lubricant selected from cationic fiber lubricants, nonionic fiber lubricants and polyoxyalkylene homopolymers and copolymers. With the polyoxyalkylene lubricants any amount of the propylene oxide moiety is less than around 80 weight percent of the copolymer to assure water solubility for aqueous based sizes. Nonexclusive examples of cationic lubricants include: oxyalkylated amines, alkyltrialkyl quaternary ammonium salts, alkyl imidazoline derivatives, pelargonic tetraalkylene pentamine derivatives, fatty amides including fatty primary amides, fatty secondary amides, methylene and ethylene bisamides and alkanolamides. Suitable examples of nonionic lubricants include fatty acids, esters such as fatty esters, wax esters, glycerol esters, glycol esters, fatty alcohol esters and those described as complex esters, fatty alcohols, paraffinic and microcrystalline waxes, polyethylenes, oxidized polyethylenes, and the like. The amount of the lubricant employed in the chemical treating composition in the present invention is an effective lubricating amount which is generally in the range of around 0.1 to 5 weight percent of the total size or around 1 to around 20 weight percent of the nonaqueous components of the size. The most suitable lubricant is a polyoxyalkylene copolymer which is a block copolymer with a majority of ethylene oxide moiety to the propylene oxide moiety. Nonexclusive examples of these lubricants are those having viscosities ranging from around 400 to around 100,000 centistokes, for instance, the polyoxyalkylene copolymer available from Union Carbide Chemical Corporation under the



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trade designation UCON 75-H-90,000, having a viscosity of 90,000 measured in centistokes is a suitable lubricant.

Also present in most aspects of the chemical treating composition is a reactable organosilane coupling agent having at least one hydrolyzed or hydrolyzable group and having the general formula of  $R''\text{-Si-(OR')}_3$  where:  $R'$  is hydrogen and/or alkoxy groups having 1 to 5 carbon atoms; and  $R''$  is an aminoalkyl, polyaminoalkyl where the alkyl group is from 1 to 6 carbon atoms, alkyl or aryl ester, glycidoxyalkyl, glycidoxyaryl or glycidoxyaraalkyl group or an isocyanato alkyl, isocyanato aryl or isocyanato araalkyl group or ureido, ureidoalkyl and ureidoaraalkyl. Suitable examples of the amino and polyamino organosilanes are found in U.S. Patent 4,728,573, which is hereby incorporated by reference, and U.S. Patent 4,394,418, which is also hereby incorporated by reference. The amount of the organofunctional silane coupling agent present in the treating composition is an effective coupling agent amount. This amount, when the organosilane is present, generally ranges from about 1 to about 10 weight percent of the solids of the size composition and from about 0.1 to about 5 weight percent of the aqueous size composition. Use of additional amounts result in further incremental improvements that are insufficient to justify the additional cost.

Also present in the treating composition is an organo functional alkoxide or hydroxide of titanium and/or zirconium where the alkoxide preferably is compatible and active in water. In nonaqueous sizings the alkoxide titanate and/or zirconate can have the general formula:

$(\text{RO})_y\text{X-(O-A-R')}_z$  I where X is titanium (Ti) or zirconium (Zr), R is hydrogen and/or a lower alkyl group with 1 to 5 carbon atoms, A is an alkylate, carboxyl, sulfonyl, phenolic, phosphate pyrophosphate or phosphite group, and  $R'$  is a short or long chain carbon group having amine or methacrylate functionality. The letters "y" and "z" represent integers,

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where y can range from 1 to 4 and z can range from 1 to 3 and (y + z) ranges from 2 to 6. In aqueous sizings the titanate and/or zirconate are preferably soluble in water without the use of surfactants and the titanate or zirconate is still active in water. By "active", it is meant that the titanate and zirconate are not fully reacted or do not have too rapid a rate of reaction with water to produce substantial amounts of titanium or zirconium dioxide. In remaining active in water, the titanate and/or zirconate can react with water but at a slow rate of reaction so as not to produce a lot of dioxides and to be still reactive with the inorganic substrate. The amount of the organotitanate and/or organozirconate is generally an amount greater than 10, but more particularly 12 or greater, parts per 100 parts of the film forming polymer.

When one or more of these salts are present without the presence of the organosilane coupling agent, the amount is an effective coupling agent amount. Generally, the ratio amounts of the titanate salt to the organosilane on a solids basis is in the range of 6:1 to 1:6. This ratio of amounts is useful when the film forming polymer is a polyurethane and/or epoxy polymer. A particularly useful ratio of the amounts is in the range of around 2:1 to around 1:2. Nonexclusive examples of the organotitanate includes alkyl amino alkoxide titanates and zirconates, and lactic acid ammonium salt derivatives of titanate and/or zirconates and organo salts of oxyacids of titanium and/or zirconium. The alkyl and alkoxide groups can have from 1 to 5 carbon atoms, and the titanate and zirconate can be of the monoalkoxy type, the coordinate type, the chelate type and/or the quat type. With reference to Formula I above these titanates and/or zirconates have y equal to at least 1 and the alkoxide includes partially or fully hydrolyzed derivatives thereof, and z is an integer up to 3 and A and R' are part of one group such as an alkanol where O in formula I is from the alcoholic or acidic oxygen and A is hydrogen or part of the carboxyl and R' is a lower alkyl group

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having 1 to 5 carbon atoms. Also included are the titanates and zirconates like acetyl acetate titanate and zirconate. It has been found that with the presence of the organotitanate and/or organozirconate in the amounts greater than those  
5 amounts typically used as antistatic agents, these compounds function to enhance promotion of adhesion when used in conjunction with organofunctional silanes. This enhancement is measured by improvement in mechanical properties of fiber reinforced plastic composite like tensile strength notched and  
10 unnotched Izods.

This enhancement can also occur with the use of the reaction product of the titanate and/or zirconate with the silane coupling agent. Such a reaction product is formed by reaction of the coupling agents in a liquid medium under mild  
15 conditions to limit the formation of high molecular weight species and preferably to favor the lower molecular weight oligomers. The liquid medium can be a solvent such as water or organic solvents like alcohols which may influence the reaction conditions of temperature and time. The reaction  
20 product in an organic solvent can be used directly if added to an aqueous treating composition or can be added to water after most of the organic solvent is removed. For water as the solvent, the reaction conditions preferably are ambient conditions to slightly elevated temperatures; for example, up  
25 to around 40 to 60 degrees Centigrade. At the elevated temperatures the time for the reaction can be on the order of minutes to hours whereas at ambient conditions the time is generally longer. Preferably at ambient conditions in water, the time of reaction is around two to four hours. It is  
30 believed without limiting the scope of the present invention that the reaction is similar to a sol-gel type of reaction. The molar ratio of the titanate and/or zirconate to the silane is generally around 2:1 to around 1:2 but preferably around 1:1. The titanates and zirconates generally are those that do  
35 not strongly or quickly react with water to produce metal

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oxides but are more stable in water although they may hydrolyze in water. The amount of the reaction product used in the size can range from a trace amount as for a lower yield product to an effective coupling agent amount.

5           Also, there may be present in the size a suitable polyoxyethylene (POE) polymer to improve the wet state strand integrity. Such a polyoxyethylene is available under the trade designation WSR-301 having a molecular weight of around 4 million or more. This POE is present in an amount in the  
10 range of about 0.05 to about 0.6 weight percent of the total solids of the size. Use of higher amounts leads to more viscous treating compositions. The POE can be dispersed or emulsified in water by any method known to those skilled in the art. Also, there may be present a reaction product  
15 obtained by reacting an alkoxyated nitrogen containing compound such as an alkoxyated fatty amine or amide with a polycarboxylic acid and then reacting the resultant product with an epoxide compound, as further described in U.S. Patent 3,459,585 (Killmeyer, et al.), which is hereby incorporated by  
20 reference. The amount of this material can range generally from around 1 to about 10 and particularly from around 1 to around 5 weight percent of the solids of the aqueous treating composition. Other additional film forming polymers, coupling agents and lubricants known to those skilled in the art can be  
25 incorporated, but their contribution to performance properties may not be substantial enough to justify the cost of their addition.

          Also present in the size is a carrier for application or disposition of the size composition onto  
30 inorganic oxide surfaces. Typically, the carrier is water although other carriers for compositions of different viscosity such as foams and gels may also be employed. Also, the carrier can be organic solvents wherein most of the size components would be soluble. These organic solvent based  
35 sizes would be applied to the inorganic oxide substrate in an

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environment to minimize the risk of fires. The preferred carrier is water in an amount to produce an aqueous size composition having a proper viscosity and solids level for application of the composition to the inorganic oxide substrate. For inorganic oxide fibers like glass fibers the total solids (nonaqueous components) of the aqueous chemical treating composition is about 1 to about 30 weight percent and preferably about 5 to 15 weight percent. In all events the amounts of the solids in the aqueous size composition for application to fibers should not exceed that amount which will cause the viscosity of the aqueous solution to be greater than about 100 centipoise at 20°C. Solutions having viscosities greater than this are difficult to apply to the glass fibers during their formation without breaking the fibers. The total solids level may be varied to accommodate different processing speeds and application efficiency. It is preferred that the viscosity of the size be between about 1 and 20 centipoise at 20°C for best results.

Preparation of the size involves adding any of the components either simultaneously or sequentially to each other with a medium degree of agitation. Generally the method of preparing the size can be any method known to those skilled in the art.

The size is applied to inorganic oxide surfaces such as ceramic and glass fibers where the major inorganic oxide component is silica. Inorganic oxide fibers like ceramic fibers may have a substantial amount of aluminum oxide, and/or alkali metal and alkaline earth metal oxides with small amounts of ferric oxide, titanium dioxide and the like. The glass substrates can be any of the glass compositions known to those skilled in the art and particularly the fiberizable glass compositions such as those known as "E-Glass" and "621-Glass" and low or free boron and/or fluorine derivatives thereof.

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The application of size to fibers is in such a manner to result in a moisture or volatile-reduced residue of the size in the range of around 0.5 to 5 weight percent based on the total weight of the fibers with the sizing composition.

5 The aqueous sizing is applied to the glass fibers during conventional forming processes to produce sized glass fibers at attenuation speeds to accommodate the addition of the proper amount of the size. The size is applied to the glass fibers before they are gathered together to form one or more

10 strands by means of an applicator known in the art to permit contact of the liquid size with the solid fiber such as a roller or belt applicator, partially submerged in the size contained in a reservoir such as the applicator shown in U.S. Patent 2,728,972, which is hereby incorporated by reference.

15 The fibers are gathered into one or more strands by a gathering shoe and either wound onto a forming package rotating at a sufficient speed to attenuate the fibers or passed to pulling rollers to attenuate the fibers and direct them into a wet chopping unit. Attenuation of the fibers is

20 from the orifices in the bushing of the glass fiber direct melting furnace or marble melting furnace for the addition of the proper amount of the size to the fibers. Other methods of applying the size to the fibers such as pad applicators may be employed. The amount of the volatile reduced residue on the

25 fibers is based on the measurement by the loss on ignition (LOI) method.

Continuous glass fiber strands wound on forming packages in annular layers or wet chop glass fiber strands are typically heated to reduce the volatiles including the

30 moisture content of the size on fibers in the strands by air drying or in any conventional drying ovens known to those skilled in the art. Usually, the temperatures are around 110°C to around 150°C, preferably around 115°C to around 130°C for a time of around 11 hours. Other equivalent temperatures

35 and times may be used to give equivalent heating or drying to

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remove a substantial amount of the volatiles including moisture from the strands. The moisture content of the heated strands is usually less than around 0.06 weight percent and constitutes the glass fibers with the residue of the size. A plurality of the strands with the size residue can be chopped in a dry chop operation or can be gathered in parallel to form a rope or a roving. The chopped strands or continuous strands or rovings or even woven rovings or mats of chopped strands and continuous strands are useful in preparing polymeric molding compounds. Particularly, these sized strands are useful in reinforcing the high performance polymers having higher processing temperatures and/or melt temperatures to produce RP products capable of use in a wider temperature range including elevated temperatures. A few nonexclusive examples of these high performance polymers were previously listed.

#### Preferred Embodiment

The size is an aqueous size having two film formers, a nonionic lubricant, amino organo-functional silane coupling agent and triethanolamine zirconate. One film former is an epoxy polymer in an oil-in-water dispersion where the epoxy is a bisphenol A type epoxy with approximately a 500 to 600 equivalent weight. The second film forming polymer is a poly(esterurethane) in an oil-in-water emulsion. The ratio of amounts of the solids of the film formers is in the range of around 4 to around 1 of the epoxy to the polyurethane. The nonionic fiber lubricant is poly(ethyleneoxide)-propylene oxide copolymer (PEO-PPO) with a low molecular weight and a viscosity of around 90,000 centistokes. The aminosilane is gamma-aminopropyltriethoxy-silane or 3-triethoxysilyl-propylamine available from Union Carbide Corporation under the trade designation A-1100 silane. The organoalkoxide titanate or zirconate is a triethanolamine zirconate available under the trade designation MPD-6212 Tyzor from DuPont de Nemours and Company that is an alkanolamine chelate now available as

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Tyzor 212 crosslinking zirconium alkoxide. This zirconate results in a sized fiber having good color. In an alternative embodiment where the color of the sized fibrous strand is less important, a triethanolamine titanate is used. The amounts of the components in the size on a solids basis are listed below for the preferred embodiment and in Table 1 at Example 2 for the use of the triethanolamine titanate.

	<u>lbs/100 Gal.</u>	<u>Solids (lbs.)</u>	<u>Wt % of Solids</u>
10 Epoxy polymer dispersion CMD-3502	49.79	29.87	43.2
Poly(esterurethane) dispersion Baybond XW-110-2	21.94	7.68	11.1
15 Gamma aminopropyltriethoxysilane (A-1100)	12.55	10.04	14.5
20 PEO-PPO lubricant (Ucon 75-H-90000)	5.51	5.51	8.0
Triethanolamine zirconate	20.08	16.06	23.2
Water	In an amount to dilute to 100 Gal.		

25

This aqueous size was prepared by adding 25 gallons of water (deionized) to a main mix tank. The epoxy dispersion was added to this main tank with stirring in a manner not to induce very much air. The PEO-PPO lubricant was added to a premix tank, and five gallons of water (deionized) at 150°F were added with stirring to dissolve the lubricant. An additional five gallons of water were added to the dissolved lubricant for cooling, and the dissolved lubricant was added to the main mix tank. Fifteen gallons of deionized water were added to a premix tank and the A-1100 was added with stirring not to induce too much air. Ten gallons of deionized water were added to a premix tank, and the triethanol amine zirconate was added with stirring so as not to induce too much water. This diluted material was stirred for 5 minutes and transferred to the diluted A-1100 mixture. The combined

40



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premix was stirred for 10 minutes and added to the main mix tank. Fifteen gallons of deionized water were added to a premix tank, and the polyurethane dispersion was added. The diluted mixture was stirred for 5 minutes and transferred to the main mix tank. The mixture in the main mix tank was diluted to 100 gallons with water and stirred for 30 minutes. The solids of the size is  $8.3 \pm 0.2$  weight percent, and the pH is around  $10.3 \pm 0.5$ . The viscosity is around  $2 \pm 1$  as measured by Brookfield LVT #1 spindle at 30 rpm at 75°F.

Application of the size to the fibers involves forming the glass fibers in a direct melt forming operation to have fiber diameters of G or K 9-13 microns. The fibers are cooled by pre-size-application sprays of water, and the size is applied to the plurality of fibers by the fibers contacting a roller-type applicator. A plurality of fibers are gathered into one or more strands and fed into a chopping device from the attenuation rollers to produce wet chopped strands. The chopped strands are collected and dried. The conditions of drying include a temperature in the range of 115°C to 130°C and a time of around 11 hours. A plurality of the dried, chopped strands having the volatile and moisture-reduced residue of the size have lengths ranging from around 1/16 to 1/4 of an inch but most preferably around 1/8 of an inch.

These fibers are useful in formulating fiber reinforced polyetherimide such as the Ultem polymers available from General Electric Company, Plastics Group, Pittsfield, Massachusetts. The fibers are combined with the PEI and formed into a ribbon by an extruder and are pelletized. The pellets are useful in injection molding of FRP parts.

30

#### Examples

Table 1 presents 20 formulations of the size utilized in the present invention including the sizes of the alternative embodiment. All of the sizes were prepared in a similar manner as those of the preferred and alternative

embodiments. The Rucothane 2011L utilized in formulation 18 is a poly(esterurethane) available from Ruco Chemical Company, New York.

T A B L E 1

Examples With Amounts in Weight Percent of Solids

Components of Size	1	2	3	4	5	6	7	8	9	10
Epoxy polymer dispersion CMD-35201 Celanese	45.5	45.5	49.9	43.5	49.9	58.6	39.1	44.2	44.2	50.9
Poly(ester urethane) Rucothane 2011L	--	--	--	--	--	--	--	--	--	--
Baybond XW-110-2	11.7	11.7	12.9	11.2	12.9	15.1	10.1	11.4	11.4	13.1
Witco 290H	--	--	--	--	--	--	--	--	--	--
Gamma-aminopropyltriethoxy silane	15.3	15.3	9.4	21.0	24.1	11.0	18.9	8.3	21.4	9.6
Glycidoxypolytrimethoxysilane	--	--	--	--	--	--	--	--	--	--
Poly(ethylene oxide-propylene oxide) copolymer lubricant UCON 90,000	8.4	8.4	3.7	3.2	3.7	4.3	13.0	14.7	14.7	16.9
Triethanolamine titanate	15.3	15.3	24.1	21.0	9.4	11.0	18.9	21.4	8.3	9.6
Poly(oxyethylene) WSR-301	0.37	--	--	--	--	--	--	--	--	--
Epoxidized polyester RD-1135B	3.8	--	--	--	--	--	--	--	--	--
Tyzor TE	--	--	--	--	--	--	--	--	--	--
MPD-6212 (Tyzor) 212	--	--	--	--	--	--	--	--	--	--
Solids gm/gal. 3388 gm	292.9	297.9	271.4	311.4	271.4	231.4	346.4	306.4	306.4	266.4
Actual Solids (weight %)	7.7	8.3	6.9	7.4	7.2	6.4	8.4	7.8	8.1	7.3

TABLE 1 (Cont'd.)

Examples With Amounts in Weight Percent of Solids

Components of Size	11	12	13	14	15	16	17	18	19	20
Epoxy polymer dispersion CMD-35201 Celanese	47.3	45.5	45.5	45.5	45.5	45.5	59.6	39.6	59.6	45.5
Poly(ester urethane) Rucothane 2011L	--	--	--	--	--	--	--	34.9	--	--
Baybond XW-110-2	12.2	--	11.7	11.7	--	--	15.1	--	15.1	11.7
Witco 290H	--	11.7	--	--	11.7	11.7	--	--	--	--
Gamma-aminopropyltriethoxy silane	15.9	15.3	15.3	15.3	15.3	15.3	20.0	20.0	--	15.3
Glycidoxypolytrimethoxysilane	--	--	--	--	--	--	--	--	20.0	--
Poly(ethylene oxide-propylene oxide) copolymer lubricant UCON 90,000	8.7	8.4	8.4	8.4	8.4	8.4	--	12.0	--	6.9
Triethanolamine titanate	15.9	15.3	--	--	--	--	20.0	20.0	20.0	0
Poly(oxyethylene) WSR-301	--	--	--	--	--	--	0.3	0.3	0.3	0.3
Epoxidized polyester RD-1135B	--	--	--	--	--	--	5.0	5.0	5.0	5.0
Tyzor TE	--	--	15.3	--	15.3	--	--	--	--	--
MPD-6212 (Tyzor) 212	--	--	--	15.3	--	15.3	--	--	--	15.3
Solids gm/gal. 3388 gm	286.4	297.9	297.9	297.9	297.9	297.9	--	--	--	--
Actual Solids (weight %)	7.8	7.64	7.94	8.13	--	--	--	--	--	--

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Table 2 presents three illustrative size formulations prepared in a similar manner to that of the preferred embodiments for the listed components of Table 2. These illustrative examples lacked the presence of an organo salt of the oxyacid of titanium and/or zirconium. Also, these examples used a nonionic lubricant different from that of the preferred embodiment.

T A B L E 2

Illustrative Examples (Ill. Eg.) of Sizes in Weight Percent of Solids				
<u>Components of Size</u>		<u>Ill. Eg. 1</u>	<u>Ill. Eg. 2</u>	<u>Ill. Eg. 3</u>
15	Epoxy polymer dispersion CMD-35201 Celanese	74.5	--	59.6
20	Poly(ester urethane) Rucothane 2011L Baybond XW-110-2	-- --	74.5 --	-- 14.9
25	Gamma-aminopropyltriethoxy silane (A 1100 silane)	20.0	20.0	20.0
	Poly(ethylene oxide-propylene oxide) copolymer lubricant UCON 90,000	0	0	0
	Triethanolamine titanate	0	0	0
30	Poly(oxyethylene) WSR-301	0.5	0.5	0.5
	Epoxidized polyester RD-1135B	5.0	5.0	5.0
35	Water	--An effective amount for application--		

Most of the size formulations of Tables 1 and 2 were applied to glass fibers in a manner similar to preferred wet chop operation or in a dry chop operation. These chopped sized glass fibers were used as reinforcement for various high temperature matrix polymers to prepare test specimens of FRP composites. These composites were made by injection molding. This involved preparing pellets of reinforcement in matrix polymer and injection molding the pellets.

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The pellets were tested for bulk density by a test developed by Dr. Johnson C. Watkins. This test involves weighing a 40 to 50 gram sample of pellets and placing the sample in a 100 ml graduated cylinder. The volume that the sample displaces is recorded as is the weight of the sample. The ratio of weight of the sample divided by the sampling volume equals the bulk density in units of grams per milliliter. The FRP test specimens were tested for tensile strength, percent elongation, flexural strength and modulus, Izods (notched and unnotched) by standard tests known to those skilled in the art. These tests are from the American Society of Testing Materials and respectively are identified as D-638, D-790 and D-256. The Izod impact tests are more fully discussed in the book "Reinforced Plastics Theory and Practice," M. W. Gaylord, 1969, Koppers Company, Inc., Pittsburgh, Pennsylvania, U.S.A., hereby incorporated by reference.

The results of these tests for molded FRP involving most of the sizes of Table 1 are presented in Table 3. Also shown in Table 3 are control samples that were molded samples prepared from pellets made with commercially available glass fibers. Control 1 utilized commercially available glass fibers having diameters of 13 microns and prepared by a dry chop operation in accordance with U.S. Patent 4,271,229. Control 2 utilized commercially available glass fibers having a diameter of 13 microns by a wet chop (direct chop) operation in accordance with U.S. Patent 4,615,716. Control 3 utilized commercially available glass fibers having diameters of 10 microns sold for reinforcement of PES and polyamide polymers.

In Table 3 the diameter of the glass fibers in Examples 1 through 16 and 18 was 13 microns. In Example 17 the diameter was 10 microns. The molded samples of Examples 1 and 3-11 were made with controls 1 and 3 as one set of experiments. These involved preparation of pellets at 60 lb/hour with a number 4 screw at 4,240 rpm. The molded

samples of Examples 2 and 12-16 were made along with molded samples with control 2 glass fibers at 50 lbs/hour, no vacuum and full shot, 1 hole die and No. 4 screw. The molded samples of Examples 17 and 18 involved preparation of pellets at 30 lbs/hour at 200 rpm. The matrix polymer for Examples 1-16 was Ultem PEI available from General Electric Company, Pittsfield, Massachusetts. Other matrix polymers were as indicated.

T A B L E 3  
(Part I)

Property of FRP Pellet	1	2	4	5	6	7	8
Pellet Density lb/ft <sup>3</sup> (30% 1/8" glass in pellet)	35.1	36.5	37.4	35.2	35.4	34.4	35.6
Matrix polymer	-----						
Property of Molded FRP							
Tensile strength (10 <sup>3</sup> psi)	23.6 <sup>1</sup>	23.8	23.8	23.2	22.7	23.8	22.1
Percent elongation	3.42 <sup>1</sup>	3.3	3.5	3.39	3.37	3.53	3.28
Flexural strength (10 <sup>3</sup> psi)	29.4 <sup>1</sup>	28.5	29.1	26.7	26.9	30.6	27.1
Flexural modulus (10 <sup>6</sup> psi)	1.29 <sup>1</sup>	1.3	1.24	1.22	1.21	1.29	1.23
Izod (notched) ft lb/in	1.39 <sup>1</sup>	1.26	1.52	1.55	1.47	1.45	1.39
Izod (unnotched)	8.7	8.1	9.1	8.3	8.1	8.5	8.2
Heat deflection temperature (264 psi)							
°C	210.5	207.4	209.9	--	--	--	--
°F	410.9	--	409.8	--	--	--	--

1 - Average of three samples

SUBSTITUTE SHEET (RULE 26)

TABLE 3 (Cont'd)

(Part I)

Property of FRP Pellet	9	10	11	Control 1	Control 3	12	13	14	15	16	Control 2
Pellet Density lb/ft <sup>3</sup> (30% 1/8" glass in pellet)	32.8	34.4	33.3	31.7	31.2	39.1	40.0	37.1	38.7	40.1	39.1
-----PEI-----											
Property of Molded FRP											
Tensile strength (10 <sup>3</sup> psi)	23.1	22.4	23.5	23.7	22.9	23.2	23.0	23.0	23.0	23.0	20.8
Percent elongation	3.36	3.28	3.47	3.47	3.36	3.2	3.2	3.3	3.2	3.3	2.9
Flexural strength (10 <sup>3</sup> psi)	28.3	28.4	28.0	29.6	27.8	27.0	27.0	27.0	27.0	28.0	26.3
Flexural modulus (10 <sup>6</sup> psi)	1.26	1.24	1.25	1.32	1.30	1.29	1.27	1.27	1.27	1.33	1.32
Izod (notched) ft lb/in	1.40	1.37	1.43	1.15	1.13	1.26	1.37	1.51	1.35	1.42	1.18
Izod (unnotched)	8.3	8.1	7.9	7.6	7.4	8.1	8.3	8.7	8.1	8.2	6.6
Heat deflection temperature (264 psi)	--	--	--	209.5	211.8	207.7	208.1	208.0	208.0	--	--
°C	--	--	--	409.1	413.2	--	--	--	--	--	--
°F	--	--	--	--	--	--	--	--	--	--	--

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T A B L E 3

(Part II)

Property of FRP Pellet	17	17	17	17	18 <sup>2</sup>	18	18
Pellet Density lb/ft <sup>3</sup> (30% 1/8" glass in pellet)	35.6	--	--	--	--	--	--
Matrix polymer	PEI	PEEK K-Fiber	PES	PEI	PEEK K-Fiber	PES	
<b>Property of Molded FRP</b>							
Tensile strength (10 <sup>3</sup> psi)	27.6	23.9	21.0	26.6	25.8	22.3	
Percent elongation	3.4	3.96	3.4	3.07	4.04	3.37	
Flexural strength (10 <sup>3</sup> psi)	--	35.9	--	--	38.1	--	
Flexural modulus (10 <sup>6</sup> psi)	--	1.4	--	--	1.48	--	
Izod (notched) ft lb/in	--	2.0	1.5	1.5	2.1	1.52	
Izod (unnotched)	10.1	--	12.0	9.2	--	11.5	
Heat deflection temperature (264 psi)	--	--	--	--	--	--	
°C	--	--	--	--	--	--	
°F	--	--	--	--	--	--	

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2 - Dry chopped strands



TABLE 3  
(Part II) - Cont'd.

Property of FRP Pellet	Control 2	Control 1	19	20	Control 1	Control 3
Pellet Density lb/ft <sup>3</sup> (30% 1/8" glass in pellet)			31.8	33.7	29.2	29.1
Matrix Polymer	PEI	PEI	PEI	PEI	PEI	PEI
<u>Property of Molded FRP</u>						
Tensile strength 10 <sup>3</sup> psi	23.3	25.6	24.6	24.4	22.2	22.3
Percent elongation	2.8	2.9	3.07	--	--	--
Flexural strength (10 <sup>3</sup> psi)	--	--	--	--	--	--
Flexural modulus (10 <sup>6</sup> psi)	--	--	--	--	--	--
Izod (notched) ft lb/in	1.39	1.33	--	2.0	1.59	1.59
Izod (unnotched)	7.6	8.0	8.4	--	--	--
Heat deflection temperature (264 psi)	--	--	--	--	--	--
°C	--	--	--	--	--	--
°F	--	--	--	--	--	--

Table 4 presents data on molded samples utilizing glass fiber strands with sizes of the illustrative examples of Table 2, controls and one example similar to example 17 of Table 1.

TABLE 4  
Mechanical Properties of Pellets and Molded Specimens of PEI with 40 Weight Percent Glass Fibers Sized With Illustrative Example Formulations or With Control Glass Fibers

Mechanical Properties	Eg. 1				Eg. 2				Eg. 3				Control 1				Control 17b			
	III.				III.				III.				III.				III.			
Bulk Density	32.6	25.2	25.8	33.9	35.6	30.3														
Tensile Strength	24.5	24.6	25.8	24.7	27.6	27.4														
Izod	1.58	1.54	1.4	1.39	1.73	1.36														
Percent Glass Wt %	40	40	40	40	40	40														

The pellets and molded specimens for testing from the pellets for the illustrative examples control and 17b were prepared in a manner similar to the preparations used for the pellets and molded specimens of Table 3. In comparing Tables 3 and 4, it is evident that the formulations and sized glass fibers of illustrative examples 1 and 2 are less than satisfactory in mechanical properties to that of the control number 1. Also, the formulation and size fiber of illustrative Example 3 is not acceptable in mechanical properties when compared to the control. The formulation 17b, number 2 from Table 3, number 14 from Table 3 and number 20 from Table 3 and glass fibers sized with these formulations gave good thermal performance as shown by the increased value for bulk density, especially over those of illustrative Examples 1 and 2. Also, these examples give good mechanical properties compared to the control. Also, formulation 14 using the organo zirconate as opposed to the organo titanate.

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of Example 2 from Table 3 gave a slight increase in the Izod impact strength while maintaining the 20 percent improvement in tensile strength over formulation of illustrative Example 3 without either the titanate or zirconate. Also, the color of the molded test bar was not as dark as the molded test bar made with the chopped, sized glass fibers of formulation 2 having the titanate. Also, formulation 20 of Table 3 shows improved fiber forming performance while maintaining the improvements of thermal resistance in the bulk density and the tensile strength previously observed for glass fibers sized with formulations having the organotitanate or zirconate along with the aminosilane coupling agent.

A long-term heat aging test was conducted on two samples of PEI matrix polymer reinforced with 30 weight percent glass fibers. One sample was PEI reinforced with sized glass fibers of the preferred embodiment, where the fiber diameter was 13 microns. The second sample was control 3, where the fiber diameter was 9 microns. The long term heat aging test was conducted by testing specimens before heat aging and by placing numerous specimens of both samples of reinforced PEI in an oven at 220°C. Specimens of both samples were withdrawn after 1,000 hours, 2,000 hours and 3,000 hours for tensile strength testing.

TABLE 5

25	<u>Property</u>	<u>Preferred Embodiment Sample</u>	<u>Control 3</u>
	Pellet density before molding	36.9	34.7
30	Heat deflection temp 264 psi	208.0	207.1
	Izod (unnotched/notched)	8.4/1.35	7.7/1.17
	Flexural modulus X10 <sup>6</sup>	1.37	1.33
	Flexural strength X10 <sup>3</sup> psi	28.7	28.8
	Percent elongation	3.2	3.2
35	Tensile strength (x10 <sup>3</sup> psi)	23.2	23.8

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		<u>(% COV)<sup>1</sup></u>	<u>(% COV)<sup>1</sup></u>
	Tensile strength (x10 <sup>3</sup> psi)		
	after 1,000 hours	15.3 (14)	17.4 (13.5)
	after 2,000 hours	18.0 (4)	19.0 (7.1)
5	after 3,000 hours	13.5 (4.2)	7.5 (8.9)

<sup>1</sup> % COV is percent coefficient of variation.

Table 5 shows the PEI reinforced with the glass  
 10 fibers of the preferred embodiment have good retention of  
 tensile strength after long term heat aging and especially  
 after 3,000 hours.

Table 6 shows the performance of the reaction  
 product of the silane coupling agent with the titanate vs. the  
 15 silane coupling agent alone for two types of silane coupling  
 agents. The results are obtained from studies of glass slides  
 that were coated with the indicated coupling agent or reaction  
 product. The reaction product of the gamma-aminopropyltri-  
 ethoxysilane and triethanolamine titanate and the reaction  
 20 product of the gamma-glycidoxypropyltrimethoxysilane and the  
 triethanolamine titanate for the studies were produced in the  
 following manner. The particular silane and titanate were  
 combined in an aqueous mixture in an amount of five grams of  
 the titanate and 5 grams of the silane per 100 grams of water  
 25 at conditions of 23 degrees Centigrade and for four hours.  
 The reaction products as well as the individual silanes  
 depicted in Table 6 were wiped onto separate glass slides with  
 cotton swabs. The slides were air dried, and the treated  
 slides were heated on a hot plate to the softening temperature  
 30 of the particular resin of Table 6 to be added to that  
 particular slide. The particular resin was pressed onto the  
 slide with an untreated glass slide, and the resin was cooled  
 for a period of 30 minutes.

The prepared slides were tested in a thin film  
 35 adhesion test for rigid polymers similar to that described in  
 the book entitled, "Silane Coupling Agents" by Edwin P.  
 Plueddemann, second edition, Plenum Press, New York, 1992 at

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pages 6-7. One difference in the test of Table 6 and that of Dr. Plueddemann was that the prepared slides were not soaked in water before attempting to loosen the film of the prepared slide with the razor blade. The scale in Table 6 is developed from testing the resin coated glass slides for adhesion. If the resin was easily lifted off the slide with the razor blade, the adhesion was indicated as being 0. If the glass actually came off the slide from the scrapping with the razor blade, a value of 4 was given to the adhesion.

TABLE 6

Resin Adhesion to Glass

Resin	A	<u>Coupling</u>		Agent <u>C+B</u>
		<u>A+B</u>	<u>C</u>	
Polyamide (Nylon 6,6)	4	-	-	-
Polybutylene terephthalate (PBT)	2	3	0	4
20 Polyethylene sulfide (PES)	3	4	0	0
Polyethyleneimine (Ultem)	3	4	1	3
Polypropylene	0	0	0	0
Polyethylene high density	2	3	0	-
Polyacetal (Delrin)	0	0	0	0
25 Polyphenyleneoxide + HIPS (Noryl)	2	4	0	4
Polyacrylate (Durel)	3	3	2	3
Polyetherketone (PEK)	3	3	0	2

HIPS = high impact polystyrene

30 A = gamma-aminopropyltriethoxysilane (A-1100)

B = tetraethanolamine titanate (TEAT)

C = gamma-glycidoxypropyltrimethoxysilane (A-187)

Scale 0 - 4

0 = wipes of glass slide

35 4 = glass came of slide

From Table 6 it is shown that in all instances the reaction product gave the same or better adhesion than the silane coupling agent alone. The amount of the silane coupling agent used in treating the glass slide was the same

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as the amount of the reaction product used in treating its glass slide. In a comparison of the values in Table 6 of the results from the individual silane or titanate coupling agent to the two reaction products an improvement in adhesion occurred in fifty percent of the tests.

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## WE CLAIM:

1. Inorganic oxide substrates treated with an aqueous chemical treating composition having an effective coupling agent amount of a reaction product of  
5 organofunctional silane coupling agent and an organo alkoxide or hydroxide of a metal selected from the group comprising titanium and zirconium reacted in an aqueous medium at mild conditions wherein the ratio of the silane to the other coupling agent is in the range of around 2:1 to around 1:2.
- 10 2. Substrates of Claim 1 wherein the aqueous medium of the reaction is the carrier for treating the substrates and is present in an effective application amount.
3. Substrates of Claim 1, which includes an sizing agent selected from the group of at least one film forming  
15 polymer present in an effective film forming amount, and at least one fiber lubricant in an effective lubricating amount and mixtures thereof.
4. Inorganic oxide substrates treated with an aqueous chemical treating composition, comprising:  
20 a. at least one film forming polymer that is essentially free of polyvinylacetate homopolymer and homopolymers and copolymers of polyacrylates and present in an effective film forming amount,  
b. at least one fiber lubricant in an  
25 effective lubricating amount,  
c. organofunctional silane coupling agent having the formula  $R''\text{-Si-(OR')}_3$ , where:  $R'$  is selected from the group consisting of hydrogen and alkoxy groups having 1 to 5 carbon atoms; and  $R''$  is selected from the group consisting  
30 of: an aminoalkyl, polyaminoalkyl or amino or polyamino alkyl or aryl ester; glycidoxyalkyl, glycidoxyaryl, or glycidoxyarylalkyl, or glycidoxy alkyl or aryl ester group; isocyanato alkyl, isocyanatoaryl or isocyanato araalkyl or isocyanato alkyl or aryl ester group; ureido, ureidoalkyl or  
35 ureidoaraalkyl or ureido alkyl or aryl ester group; where the

alkyl group is from 1 to 6 carbon atoms; and mixtures of these organofunctional silane coupling agents present in an amount ranging from 0 to 5 weight percent of the aqueous chemical treating composition which is an effective coupling agent amount, wherein the amount is zero when the film forming polymer is selected from an epoxy polyurethane copolymer and two film forming polymers, where one is an epoxy-containing polymer and the other is a polyurethane and they are present in a ratio in the range of around 6 to 1 to around 1 to 6,

10 d. organo alkoxide or hydroxide of a metal selected from the group consisting of: titanium and zirconium, present in an amount as the salt in a range from 12 parts per 100 parts of the film-forming polymer to be amounts greater than those amounts used for antistatic agents, and up to at least an effective coupling agent amount, and wherein when the organofunctional silane coupling agent is present the ratio of amounts of the organoalkoxide of the metal to the organofunctional silane is in the range of about 2 to 1 to around 1 to 1; and

20 e. a carrier for application of the chemical treatment to the substrate present in an effective application amount.

5. Chemically treated inorganic oxide fibers having the chemical treatment, comprising:

25 a. polyurethane film forming polymer in an effective film forming amount for fibers that are contacted with matrix polymers selected from the group consisting of polyphenylenesulfide, polyetherimide, polyacrylates and polyamide,

30 b. at least one fiber lubricant in an effective lubricating amount and essentially free of large amounts of propylene oxide moieties,

c. organofunctional silane coupling agent in an effective coupling amount,



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d. organo alkoxide of a metal selected from the group comprising titanium and zirconium that is water compatible and active in water and present in a ratio of amounts with the organosilane in the range of 6:1 to 1:6; and

5 e. a carrier for application of the chemical treatment to the fiber present in an effective application amount.

6. Fibers of Claim 5, which includes an epoxy functional compound selected from the group comprising  
10 copolymer with the diisocyanate monomer; polyurethane dimer, oligomer, and film-forming polymer in a ratio of amounts ranging from around 10:1 to around 1:10 with the polyurethane polymer.

7. Fibers of Claim 5 wherein the epoxy  
15 functionality is present as a second film-forming polymer in a ratio of amounts with the polyurethane polymer of around 1 to around 4.

8. Treated inorganic oxide substrates of Claim 4 wherein the substrates are fibers.

20 9. Chemically treated inorganic oxide fibers of Claim 5 where the fibers are glass fibers.

10. Chemically treated glass fibers having a volatile-reduced residue of a chemical treating composition comprising:

25 a. one film forming polymer that is an epoxy polymer present as a liquid, solution, emulsion, dispersion or suspension,

b. another film forming polymer that is a polyurethane film forming polymer selected from the group  
30 comprising: polyurethane polymers, poly(ureaurethane) polymers, poly(esterurethane) polymers, poly(esterurethane-urea) polymers and poly(etherurethane) polymers present as a liquid, solution, emulsion, dispersion or suspension, wherein the ratio of amounts of the epoxy polymer to the polyurethane  
35 polymer is in the range of around 1 to 10 to around 10 to 1

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and the total amount of the film forming polymer is an effective film forming amount,

c. at least one fiber lubricant in an effective lubricating amount,

5 d. an organo alkoxide of a metal selected from the group of titanium, zirconium and mixtures thereof that is present in an amount in the range of greater than 10 parts per 100 parts of film forming polymer to at least an effective coupling agent amount, and

10 e. a carrier for application of the chemical treatment to the glass fibers present in an effective application amount.

11. Chemically treated glass fibers of Claim 10 wherein the epoxy polymer is an epoxy polymer dispersion with  
15 a weight per epoxide of around 500 to 600 and a viscosity of around 8,000 to 12,000.

12. Chemically treated glass fibers of Claim 10 wherein the polyurethane is an oil-in-water dispersion of poly(esterurethane) having little, if any, free isocyanates  
20 and having film properties of tensile strength ranging from 4,500 to 6,600 psi and a percent elongation of around 170 percent to 720 percent at break and a modulus at 100 percent elongation ranging from 250 psi to around 5,200 psi.

13. Chemically treated glass fibers of Claim 10  
25 having at least one organofunctional silane coupling agent present in an amount in the range of 0.1 weight percent of the solids of the chemical treating composition to an effective coupling agent amount.

14. Chemically treated glass fibers of Claim 13  
30 wherein the ratio of amounts of the organo alkoxide of the metal to the organofunctional silane coupling agent ranges from around 6 to 1 to around 1 to 6.

15. Chemically treated glass fibers of Claim 10 wherein the carrier is water in an amount to produce a  
35 viscosity for the aqueous chemical treating composition of

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less than around 100 centipoise and wherein the titanate and/or zirconate are water compatible and active in aqueous solutions.

16. Chemically treated glass fibers of Claim 15 wherein the organo alkoxide of a metal is selected from trialkanolamine titanate and trialkanolamine zirconate where the alkyl group has carbon atoms ranging from 1 to 5.

17. Chemically treated glass fibers of Claim 10 wherein the total film forming amount is in the range of around 1 to around 25 weight percent of the aqueous chemical treating composition.

18. Chemically treated glass fibers of Claim 10 wherein the fibers are in the form of chopped strands comprised of a plurality of the fibers.

19. Chemically treated glass fibers as chopped strands present in a matrix polymer selected from the group consisting of polyphenylene sulfide, polyethylene imine, polyacrylates, polyethersulfone, polyaromatic ketones including polyetheretherketone, polyetherketone, polyetherketone-ketone and polyketone.

20. Chemically treated glass fibers having a volatile-reduced residue of an aqueous chemical treating composition comprising:

a. one film forming polymer which is an epoxy polymer having an equivalent weight per epoxide in the range of 500 to 600 present in an oil-in-water emulsion,

b. a polyesterpolyurethane film forming polymer present in an oil-in-water dispersion, wherein the total amount of the film forming polymer is in the range of around 1 to around 25 weight percent of the aqueous chemical treating composition and the ratio of amounts of the epoxy polymer to the polyurethane polymer is around 4 to 1 to around 1 to 4,

c. at least one nonionic fiber lubricant selected from polyethylene oxide-polypropylene oxide

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copolymers wherein the amount of propylene oxide moieties does not exceed around 80 weight percent of the copolymer and in a viscosity range of around 400 to 100,000 centistokes present in an amount in the range of around 1 to around 20 weight percent of the nonaqueous components of the aqueous chemical treating composition,

d. an organofunctional silane coupling agent having organic functionality selected from the group of amine, polyamine, epoxy, and ureido functionality wherein the amount of the organofunctional silane coupling agent ranges up to around an effective coupling agent amount,

e. at least one organo alkoxide of a metal selected from the group comprising trialkanolamine titanate and trialkanolamine zirconate including triethanolamine titanate and triethanolamine zirconate, and

f. water in an effective amount to give a viscosity for the aqueous chemical treating composition of less than around 100 centipoise at 20°C.

21. Chemically treated glass fibers of Claim 20 wherein the aqueous chemical treating composition includes a reaction product obtained by reacting an alkoxyated nitrogen-containing compound including an alkoxyated fatty amine or amide with a polycarboxylic acid and further reacting the resultant product with an epoxide compound present in an amount in the range of around 1 to around 10 weight percent of the solids of the aqueous chemical treating composition, and a polyoxyethylene polymer having a molecular weight of around 4 million or more present in an amount of around 0.05 to about 0.6 weight percent of the aqueous chemical treating composition.

22. Chemically treated glass fibers of Claim 10 wherein the fiber lubricant is a nonionic lubricant selected from the group consisting of polyoxyalkylene homopolymers, polyoxyalkylene copolymers including polyethylene oxide-polypropylene oxide copolymers having less than around 80

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weight percent of the copolymer comprised of the propylene oxide moiety having viscosities from around 400 to around 100,000 centistokes, paraffinic and microcrystalline waxes, polyethylenes, oxidized polyethylenes, wax esters and glycerol esters and fatty alcohol esters.

23. Chemically treated glass fibers of Claim 18, 20 wherein the fibers are present in chopped strands comprising a plurality of the fibers.

24. Treated inorganic oxide substrates of Claim 1, 10 wherein the substrates are fibers and the organo alkoxide of titanium and zirconium metal is selected from the group consisting of alkoxide titanate and zirconate having the Formula I of:  $(RO)_y-X-(OAR')_z$  where X is titanium or zirconium, R is hydrogen, lower alkyl group with 1 to 5 carbon 15 atoms, A is an alkylate, carboxyl, sulfonyl, phenolic, phosphate, pyrophosphate, or phosphite group; and R' is a short or long chain carbon group having amine or methacrylate functionality and y and z are integers, where y can range from 1 to 4 and z can range from 1 to 3 and  $(y + z)$  ranges from 2 20 to 6.

25. Treated inorganic oxide substrates of Claim 24 wherein the alkoxide titanate and zirconate of Formula I have y equal to at least 1 and the alkoxide includes partially and fully hydrolyzed derivatives thereof and z is an integer up to 25 3 and A and R' are part of one group that can be an alkanol, where O in Formula I is from the alcoholic or acidic oxygen and A is hydrogen or part of the carboxyl and R' is a lower alkyl group having 1 to 5 carbon atoms.

26. Treated inorganic oxide substrates of Claim 1 30 wherein the titanate and zirconate are selected from the group consisting of: alkyl amino alkoxide and/or hydroxide titanates and zirconates, and lactic acid ammonium salt derivatives of titanate and/or zirconates and organo salts of oxyacids of titanate and/or zirconium, wherein the alkyl and 35 alkoxide groups can have from 1 to 5 carbon atoms.

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27. Treated inorganic oxide substrates of Claim 4 wherein the at least one film forming polymer is selected from the group consisting of: epoxy polymer; polyurethane film forming polymer selected from the group consisting of:

5 poly(ureaurethane) polymers, poly(esterurethane) polymers, poly(esterurethaneurea) polymers and poly(etherurethane) polymers; epoxy-polyurethane copolymers; bisphenol A thermoplastic polyesters; and polyvinylpyrrolidone, wherein the polymers can be present as a liquid, solution, emulsion,

10 dispersion or suspension.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/00574

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>																				
IPC(5) : D02G 3/00; B32B 9/00, 25/20; C08L 75/00, 83/00; C08K 3/20 US CL : 428/373, 375, 378, 391; 524/588, 591 According to International Patent Classification (IPC) or to both national classification and IPC																				
<b>B. FIELDS SEARCHED</b>																				
Minimum documentation searched (classification system followed by classification symbols) U.S. : 428/373, 375, 378, 391; 524/588, 591																				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched																				
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)																				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>																				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																		
X	US, A, 4,615,946 (TEMPLE) 07 OCTOBER 1986, col. 1, lines 5-12.	19																		
X ---- Y	US, A, 3,920,596 (FURUKAWA et al.) 18 NOVEMBER 1975, Example 1; col. 4-6.	1-3 & 24-26 ----- 4 & 8																		
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.																				
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* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention																		
*A document defining the general state of the art which is not considered to be part of particular relevance	*X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone																		
*E earlier document published on or after the international filing date	*Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art																		
*L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G	document member of the same patent family																		
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*P document published prior to the international filing date but later than the priority date claimed																				
Date of the actual completion of the international search 01 MARCH 1994		Date of mailing of the international search report 24 MAR 1994																		
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